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AUTHOR(S):

Sakamoto, Hirotoishi; Matsuda, Ryotaro; Kitagawa, Susumu

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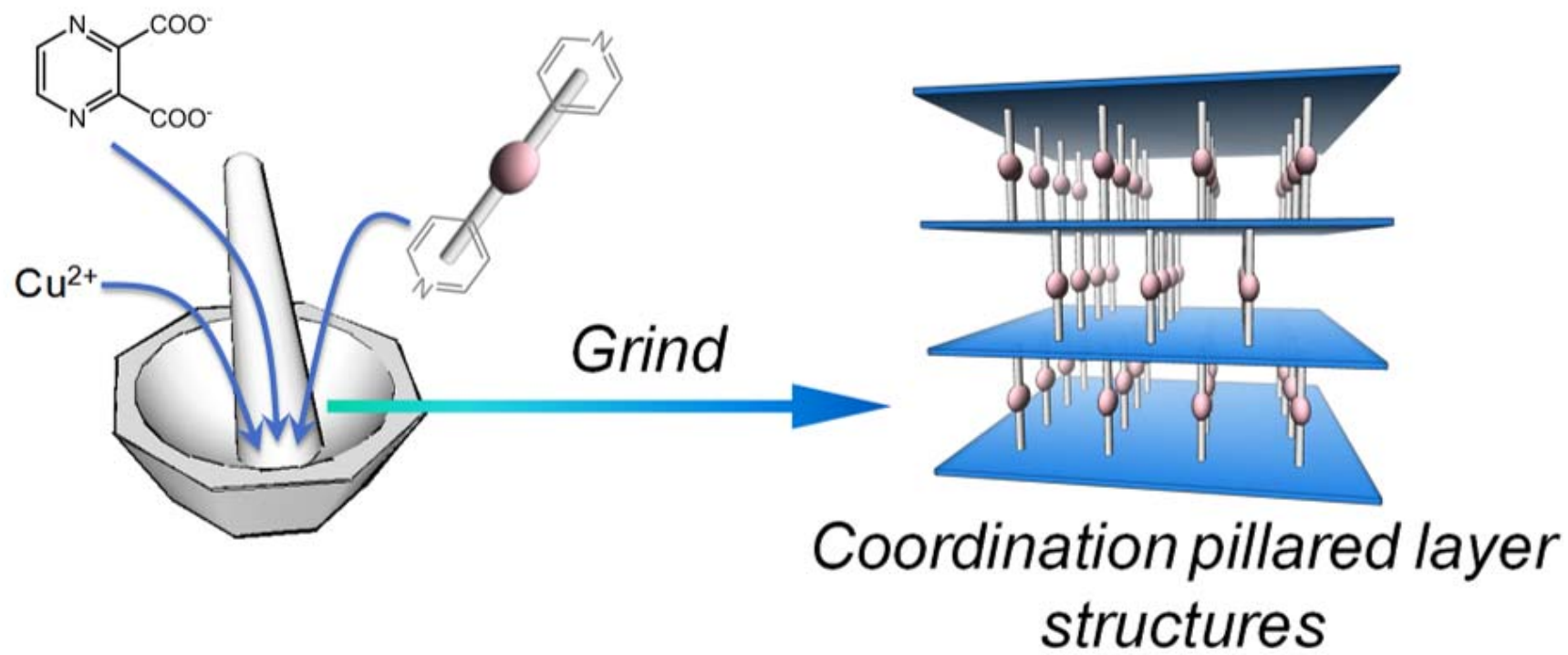
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Systematic mechanochemical preparation of a series of coordination pillared layer frameworks

Hirotohi Sakamoto,^{a,b} Ryotaro Matsuda^{b,c} and Susumu Kitagawa^{*a,b,c}

A detailed investigation into the mechanochemical synthesis of coordination pillared-layer frameworks (CPLs), particularly **CPL-1**, was carried out. In the case of **CPL-1**, a two-step reaction was observed (from the starting reactants to the final product). In the conventional solution process, no intermediate state was detected. We found that moisture is essential in both the reaction steps. After the final product was washed, it showed the same sorption ability as the product prepared from solution process. We further demonstrated the systematic preparation of other CPLs (**CPL-2**, **3**, **4**, **5**, and **15**) by the mechanochemical method under humid conditions, even though some of the ligands are almost insoluble in water. Our findings indicate that mechanochemical synthesis is a promising alternative method for the systematic and large-scale production of PCPs. Its advantages include the following: reduced pollution, low cost, simplicity of the process, ease of handling, efficient reaction rate, selectivity, and the issue of low solubility of reactants is overcome.

Introduction

Porous coordination polymers (PCPs) constructed from transition metal ions and bridging ligands have become widely known as a new class of microporous materials¹⁻⁵ because of their wide range of potential applications such as gas storage,⁶ separation,⁷ heterogeneous catalysis,^{8,9} and others. To date, most PCPs have been synthesized by mixing metal ions and ligands in solution at room temperature or under hydro/solvothermal conditions.¹⁰ However, in these processes, large volumes of solvent

are required to produce bulk quantities of the PCP materials for industrial use, which is environmentally unfavourable and makes the products costly. To overcome this problem, much effort has been made to develop alternative preparation methods, such as ionothermal,¹¹ electrochemical,¹² sonochemical,¹³ and microwave¹⁴ methods, amongst others.

The mechanochemical method—mechanical mixing of starting materials appears to be a promising technique.^{8, 15-22} Mechanochemical syntheses have many advantages: reducing pollution, low cost, simplicity of the process, ease handling, efficient reaction rate, selectivity,²³ and the issue of low solubility of reactants is overcome. These factors are especially important in industry.^{18,24} However, to date, the application and versatility of such mechanochemical methods for the synthesis of PCPs has been limited, and not been thoroughly investigated. We therefore considered it is worth investigating the applicability of the mechanochemical method to synthesis of PCPs.²⁵

The frameworks of PCPs can be systematically designed by the proper choice of their building blocks. PCPs with various pore sizes, shapes and surface properties have been synthesized.^{3, 26} Previously, we reported a PCPs referred to as coordination pillared-layer (CPL) structures. CPLs are constructed from neutral 2D layers composed of Cu^{II} and pyrazine-2,3-dicarboxylate (pzdc) which are further pillared by various dipyriddy bridging ligands (L) to form 3D frameworks [Cu₂(pzdc)₂(L)]_n with 1D microporous channels and, more importantly, with the same connectivity of the components²⁷⁻³¹. Because of the wide variety of CPLs, they are suitable for the systematic investigation of mechanochemical syntheses.

Herein, we applied the mechanochemical method to the CPL system to demonstrate the suitability for the syntheses of PCPs. During the preparation of **CPL-1**, a two-step reaction was observed (from the reactants to the final product). An intermediate state was not detected during in a conventional solution process. We also revealed that moisture is essential in both steps and that the product shows the same sorption ability after washing treatment. We further demonstrated the systematic preparation of other CPLs (**CPL-2**, **3**, **4**, **5**, and **15**, see Scheme 1) by the

mechanochemical method under humid conditions. Subsequently, we were able to obtain some insight into the formation mechanism of CPLs.

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Scheme 1

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Results and discussion

Mechanochemical synthesis of CPL-1

We carried out the mechanochemical mixing of copper(II) nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, 0.5 mmol), disodium pyrazine-2,3-dicarboxylate (Na_2pzdc , 0.5 mmol), and pyrazine (pyz, 12.5 mmol) using the same ratio of reactants as used in the solution process.²⁷ These reactants were ground together with a pestle in an agate mortar for twenty minutes and a greenish blue powder (intermediate phase **M**) was obtained. The colour and the X-ray powder diffraction (XRPD) pattern of the powder product were different from those of **CPL-1**, which is indicative of no formation of **CPL-1**. After allowing the powder to stand in air for one day, the colour changed to the sky blue of **CPL-1**. The XRPD pattern of **CPL-1** showed characteristic peaks, with some impurity peaks, indicating that **CPL-1** was spontaneously produced by the method in a multiple-step process. The XRPD patterns are shown in Fig. 1, together with a simulated pattern from a single crystal structure and that of **CPL-1** prepared by the solution process.

<< insert figure and caption

Fig. 1 XRPD patterns of (a) simulation from crystal structure of **CPL-1**, (b) **CPL-1** prepared in solution process, (c) the product mixture of the components after grinding for 20 min., (d) the

mixture left in air for 1 day, and (e) 2 days. And the picture images of (c) and (d).

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To identify the greenish blue intermediate product **M**, we compared its XRPD pattern with those of all the reactants and the binary combinations of them as shown in Fig. 2. We found that the main impurity in the residual solid was assignable to $\text{Na}(\text{NO}_3)$ which was formed from the $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and Na_2pzdc . It is worth noting that the XRPD pattern of **M** was neither the simple superposition of each single reactant, nor any binary products of the reactants. This result indicates that **M** contains a specific new phase that formed during the mechanochemical reaction of the three reactants—it is not simply a mixture of them.

<< insert figure and caption

Fig. 2 XRPD patterns of single components of **CPL-1**, disodium nitrate, the binary mechanochemical products, and the ternary mechanochemical product **M**.

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Humidity dependency on the transitions

We tried to determine the transition behaviour from **M** to **CPL-1** by observing the time course of XRPD patterns of the reaction mixture (Fig. S1 in supporting information). Only slight changes, and no production of **CPL-1**, were observed after 12 h in the chamber of the XRPD instrument, the humidity of which is lower than that of air. However, leaving the measured sample in air for a further 12 h afforded the pattern of **CPL-1**. These observations gave us the idea that humidity might be essential for the transition.

We then examined the humidity dependency on the transition from **M** to **CPL-1** under controlled conditions, as follows: the sample containing **M** was placed in

closed systems of different humidities, one of almost 100% RH with a small amount of water, one of almost 0% RH with dry nitrogen gas.

The XRPD patterns of the sample in almost 100% RH and 0% RH were measured after 5 h and 60 h, respectively. In the case of high humidity, the colour of the powder quickly changed to the sky blue colour of **CPL-1** and the patterns of **CPL-1** appeared after 5 h. The reaction was complete after 60 h, as shown in Fig. 3a. On the other hand, in the case of low humidity, no appreciable changes in the colour and XRPD pattern were observed, even after 60 h. After 60 h, the sample was removed from the dry conditions and placed in air with ambient humidity. Its colour and XRPD pattern then changed to those of **CPL-1** within 1 h, as shown in Fig. 3b. These results clearly show that water vapour facilitates the transition from **M** to **CPL-1**.

<< insert figure and caption

Fig. 3 XRPD patterns of **M** in (a) high humidity condition (~100% RH) and (b) low humidity condition (~0% RH).

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We also investigated the effect of water on the first step of the mechanochemical preparation of **CPL-1**—the transition from the starting reactants to **M**. Before mixing, the starting materials were dried using heat and vacuum to remove water from them. In this process, $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ changed into its dehydrated form. Then, to achieve completely dry operating conditions, the dried reactants were placed in a glove box and ground together using a mortar and pestle. As shown in Fig. 4, the XRPD pattern of the mixture after grinding was not that of **M**, but a simple superposition of the patterns of the three reactants, indicating that no mechanochemical reaction had occurred during the grinding process. After standing in air for 10 h, the mixture showed a pattern in which the peaks of pyz disappeared from the initial pattern because of the sublimation of pyz. The NaNO_3 impurity was not detected in the product after completely dry mixing, indicating no mechanochemical reaction between Na_2pzdc and

Cu(NO₃) in this step. After the addition of one drop of water to the mixture, the powder dissolved and the diffraction peaks weakened, indicating that the water-soluble reactants remained unchanged. This also indicated that the dried reactants do not react mechanochemically at all—in other words, water is essential also for initiating the formation of **M**.

<< insert figure and caption

Fig. 4 XRPD patterns of the mixture of dried components of CPL-1 (a) just after mixing, (b) left in air for 10 h, and (c) with one drop of water

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Washing treatment and adsorption measurement

As mentioned above, the as-prepared product contained NaNO₃ as an impurity, formed during the mechanochemical process. Conveniently, this impurity could be completely washed out using small volumes of methanol. This was confirmed by XRPD measurements, as shown in Fig 5. N₂ adsorption isotherms, measured at 77 K after degassing treatment at 393 K for 12 h, are shown in Fig. 6. The as-synthesized sample exhibited almost no adsorption due to the presence of an impurity. However, a sample washed with methanol exhibited the type I isotherm, with almost the same profile and in the same amount as that of **CPL-1** prepared by a solution process. There are a few examples of mechanochemically prepared PCPs with permanent porosity actually confirmed by the gas adsorption method.³²⁻³⁵ In a higher relative pressure region, small differences in the amounts of adsorption were observed. This may be attributed to the differences in their particle sizes, which affords the interstitial pores for adsorption between microcrystalline particles. We found that it was possible to control the particle sizes, depending on the conditions of grinding. Although solvent is required to remove impurities, the volume thereof is much lower than otherwise required in the solution process.

<< insert figure and caption

Fig. 5 XRPD patterns of (a) **CPL-1** prepared in solution process, (b) mechanochemically as-prepared product, (c) mechanochemical product after MeOH washing.

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<< insert figure and caption

Fig. 6 N₂ adsorption isotherms at 77 K of (a) **CPL-1** prepared in solution process, (b) mechanochemically as-prepared product, (c) mechanochemical product after MeOH washing.

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Mechanochemical syntheses of other CPLs

The mechanochemical preparation of other CPLs was also investigated to demonstrate further the suitability of this process for preparing PCPs. A procedure similar to that used for the preparation of CPL was carried out, using different pillar ligands: 4,4'-bipyridine for **CPL-2**; 2,7-diazapyrene for **CPL-3**; 1,2-azopyridine for **CPL-4**; 1,2-di(4-pyridyl)ethylene for **CPL-5**; and Cu(pyac)₂ for **CPL-15**. The following stoichiometric mixing ratio was used: Cu(NO₃)₂: Na₂pzdc: pillar ligand = 2: 2: 1 (Scheme 1).

According to the XRPD patterns shown in Fig. 7, **CPL-2**, **3**, **4**, and **5** were successfully prepared by the mechanochemical process. Of particular interest was that **CPL-15** was formed by the mechanochemical process without any organic solvent. The pillar metalloligand Cu(pyac)₂ is insoluble in water and common organic solvents, except THF and DMF (Fig. 8). Although the resulting mixtures contained NaNO₃ as a by-product, it could be removed by washing with a suitable solvent in the same manner as **CPL-1**. It was interesting to note the emergence of intermediate phases in the CPLs; shortly after grinding **CPL-1** and **15** exhibited different XRPD patterns to those of the final, but **CPL-2**, **3**, **4**, and **5** did not. These observations can be related to the rate of

product formation in the solution process, i.e., **CPL-1** and **15** were slow; **CPL-2**, **3**, **4**, and **5** were fast, which depends on the coordination ability of the pillar ligands.

<< insert figure and caption

Fig. 7 XRPD patterns of mechanochemically prepared (a) **CPL-2**, (b) **CPL-3**, (c) **CPL-4**, and (d) **CPL-5**, together with those from solution process.

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<< insert figure and caption

Fig. 8 XRPD patterns of **CPL-15** prepared by mechanochemical process together with that by solution process.

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Proposed formation process

Our observations thus far are summarized in Scheme 2. An important finding was that water molecules play the role of materials transporters in an inter- or intraparticle fashion in each step of the mechanochemical process. This can be regarded as kneading¹⁹ or liquid-assisted grinding.³⁶ It is envisaged that the water vapour or the crystal water of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ affords a diffusion-assisting phase among the reactant particles (including insoluble $\text{Cu}(\text{pyac})_2$ for **CPL-15**).²⁰ This water-assisted, interparticle diffusion is efficiently facilitated by the dynamic mechanical mixing that affords more frequent contact of the particles with their increased contact surfaces, resulting in the generation of the ternary intermediate **M** (*Step 1*). Mixing the solid reactants without grinding did not afford any products due to the low efficiency of interparticle contact. Once **M** is produced, the transformation of **M** to **CPL** proceeds, even though the precursor **M** remains static (*Step 2*). Therefore, it is proposed that the transformation is an intraparticle event and that the water molecules facilitate mobility

of the species in a particle, which is required for the formation of coordination frameworks.

<< insert

Scheme 2

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Conclusions

In this study, we carried out the systematic preparation of a series of porous CPL frameworks using the mechanochemical method as an alternative synthetic method for PCPs. During the mechanochemical preparation of **CPL-1**, we found the intermediate phase **M**, which can be regarded as a precursor of **CPL-1**, and which cannot be seen in the solution process, indicating that the process involves two steps. In both steps, water molecules play a crucial role in the construction of the PCP. It is suggested that they act as material transporters and facilitate diffusion of the species in inter- and intraparticle fashion in each step, respectively. This method is also applicable to CPLs other than **CPL-1**. Regardless of the insolubility of the pillar ligands in water, **CPL-15** can be produced without THF solvent. Our findings offer a more efficient and green route for the production of PCPs, and contribute to a better understand of the formation mechanism of PCPs.

Notes and references

^a*Department of Synthetic Chemistry and Biological Chemistry Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan). Fax: (+81) 75-383-2732; Tel: (+81) 75-383-2733; E-mail: kitagawa@sbchem.kyoto-u.ac.jp*

^b*ERATO Kitagawa Integrated Pores Project (Japan), Japan Science and Technology Agency (JST), Kyoto Research Park Bldg #3, Shimogyo-ku, Kyoto, 600-8815 (Japan)*

^c*Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501 (Japan)*

[†]*Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/*

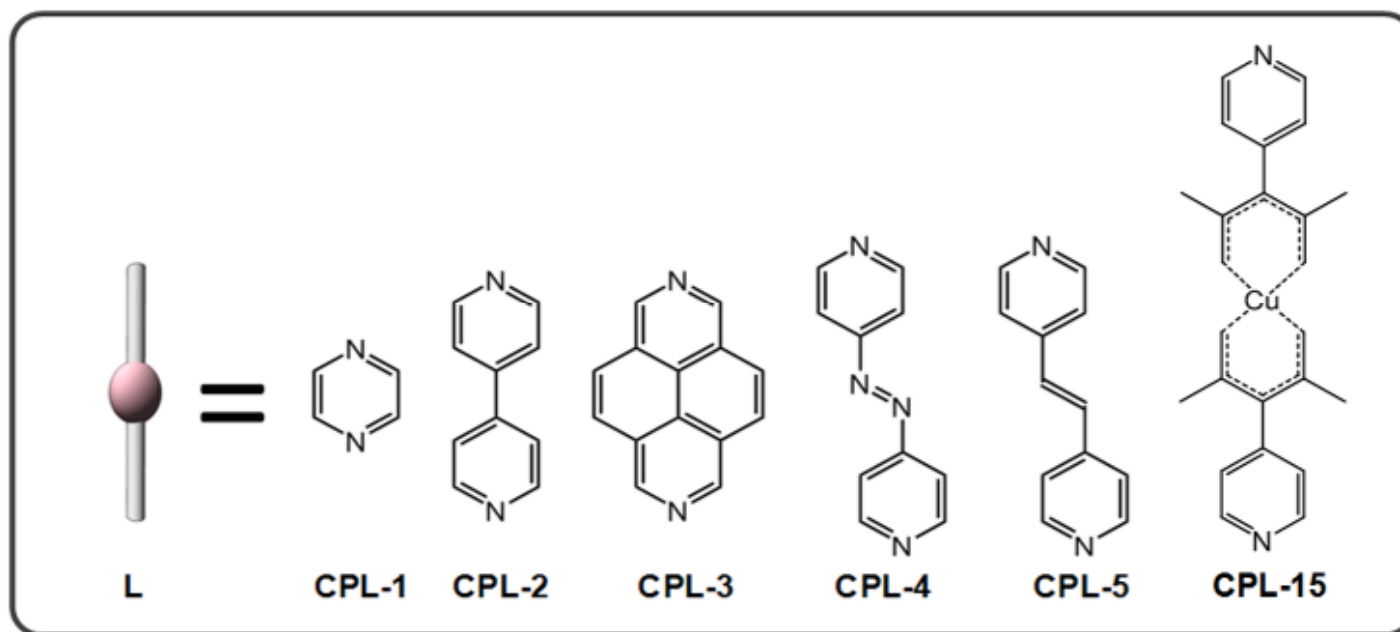
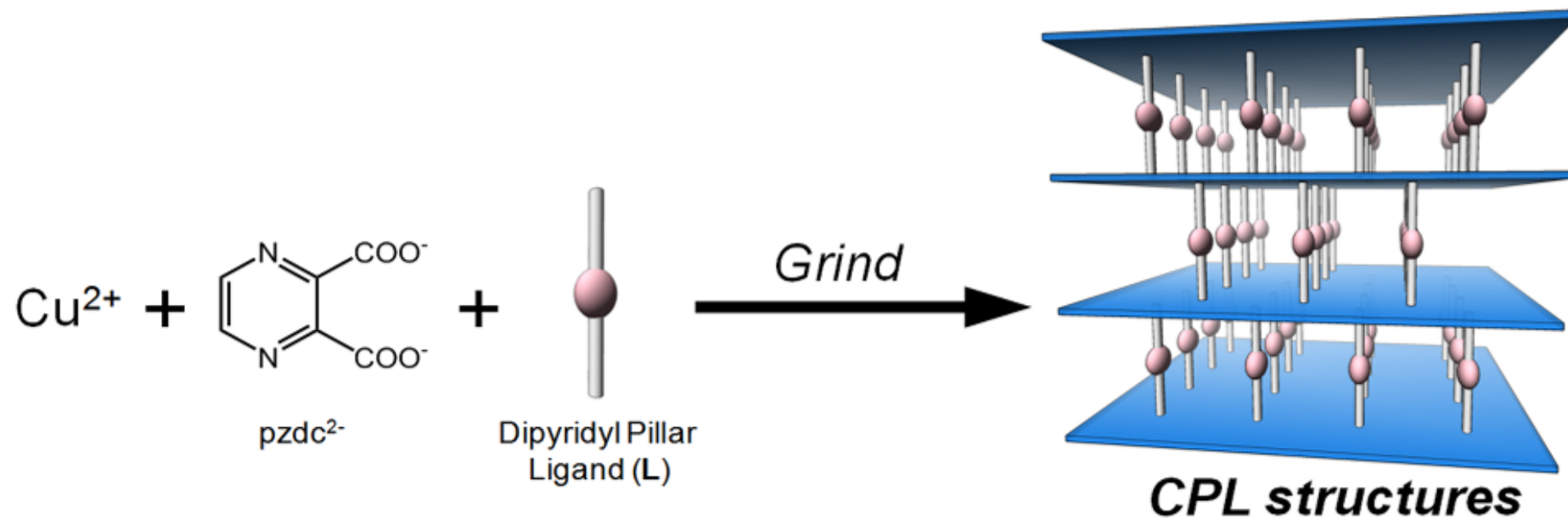
[‡] *Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.*

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Scheme 1



Scheme 2

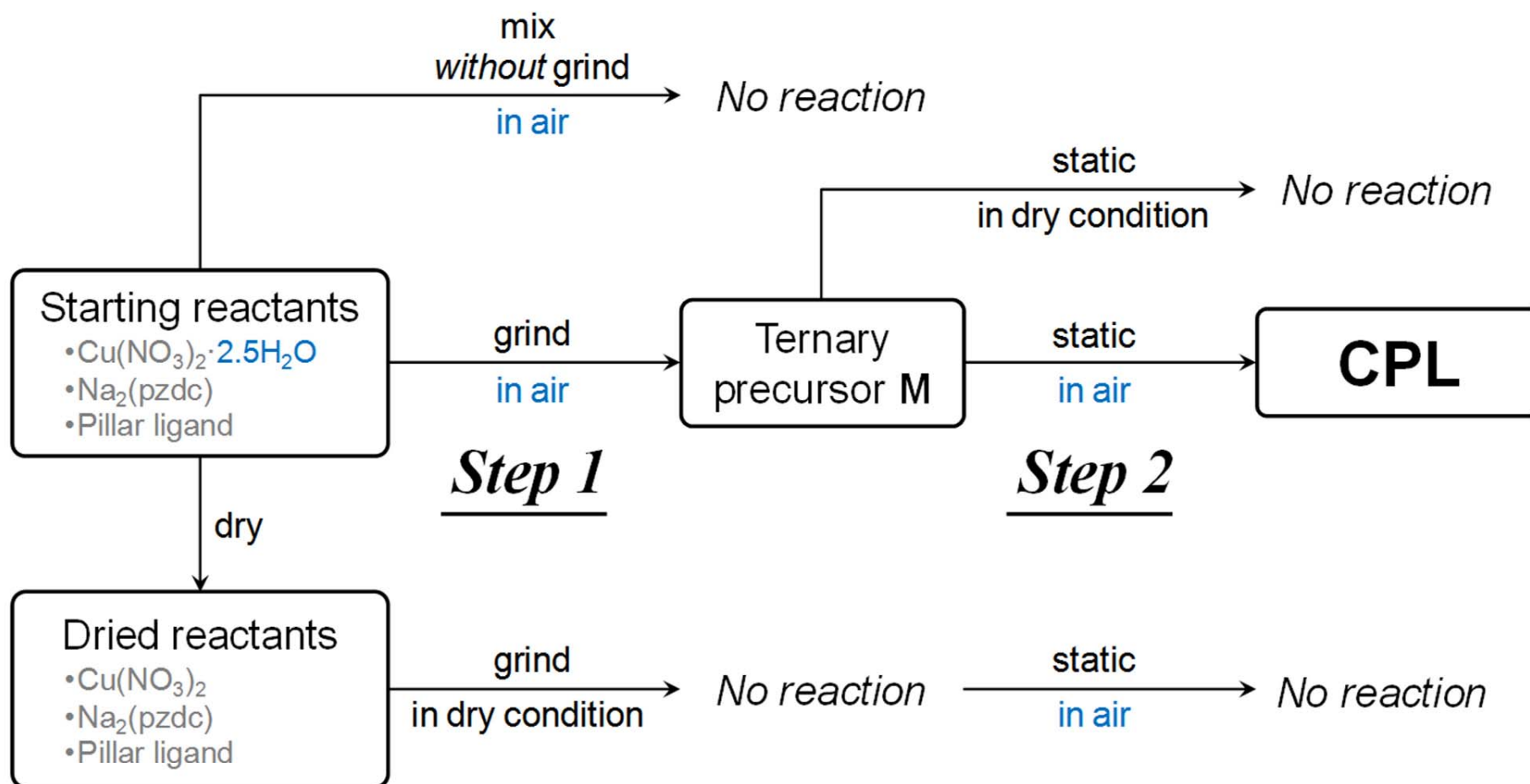


Fig. 1

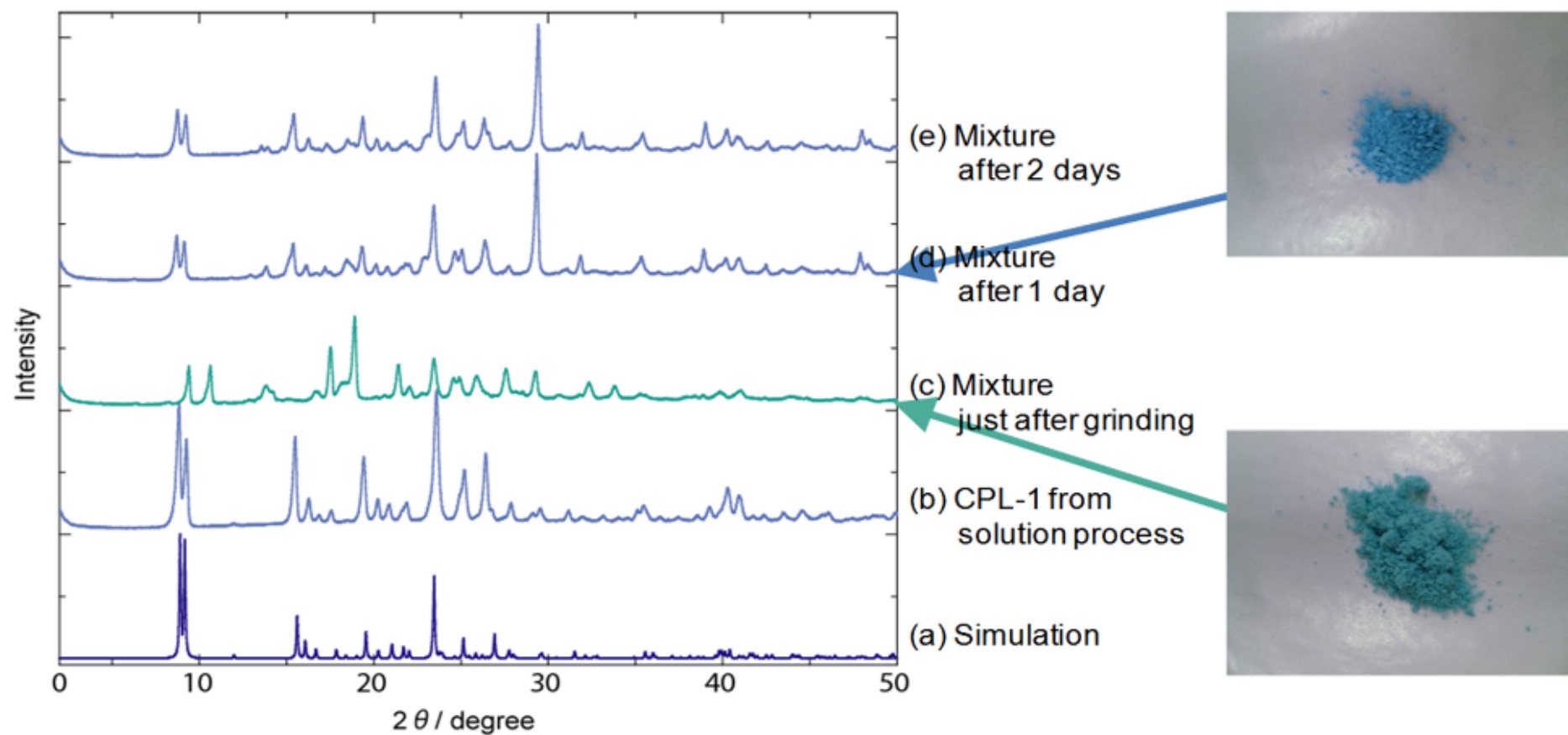


Fig. 2

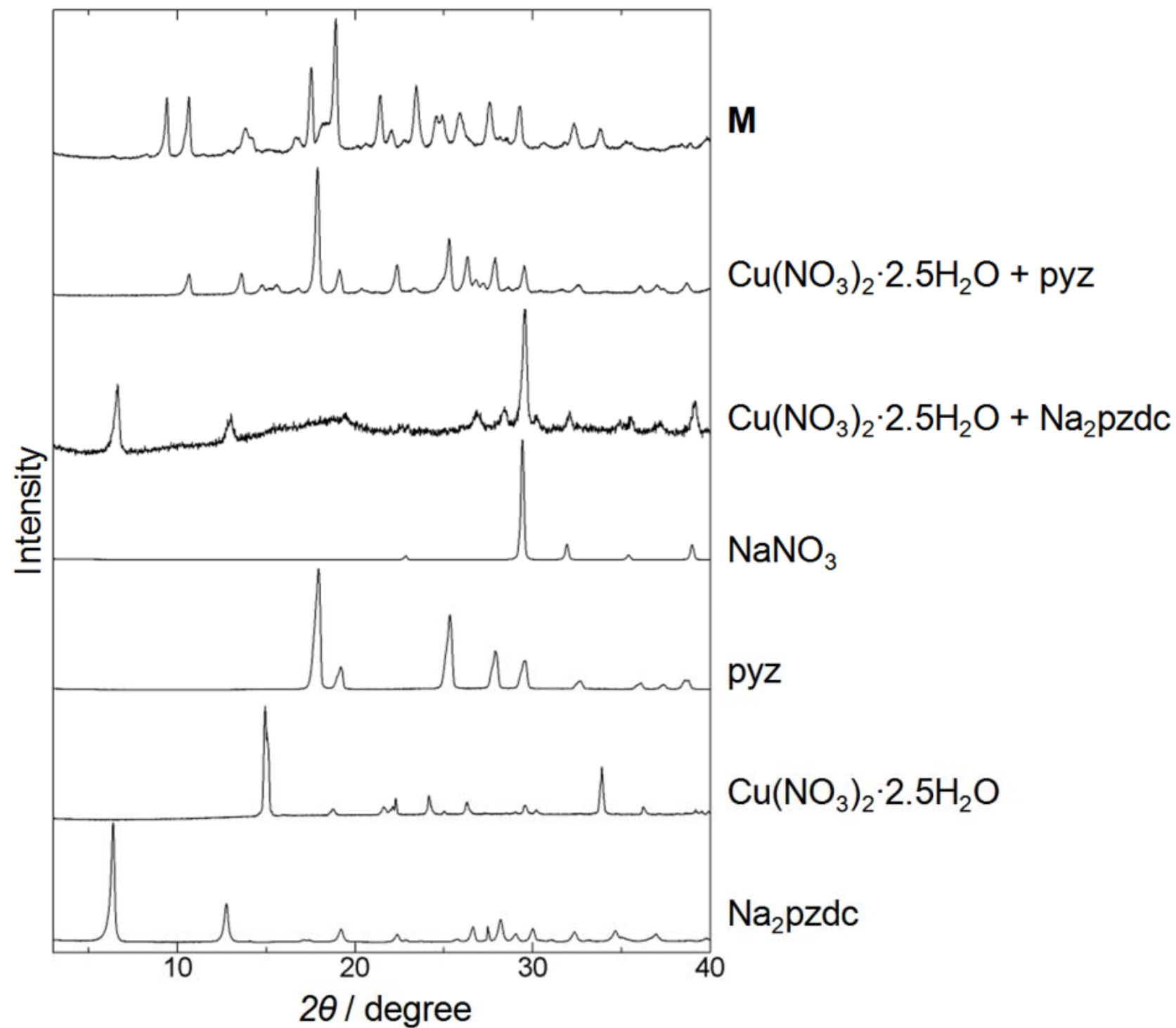
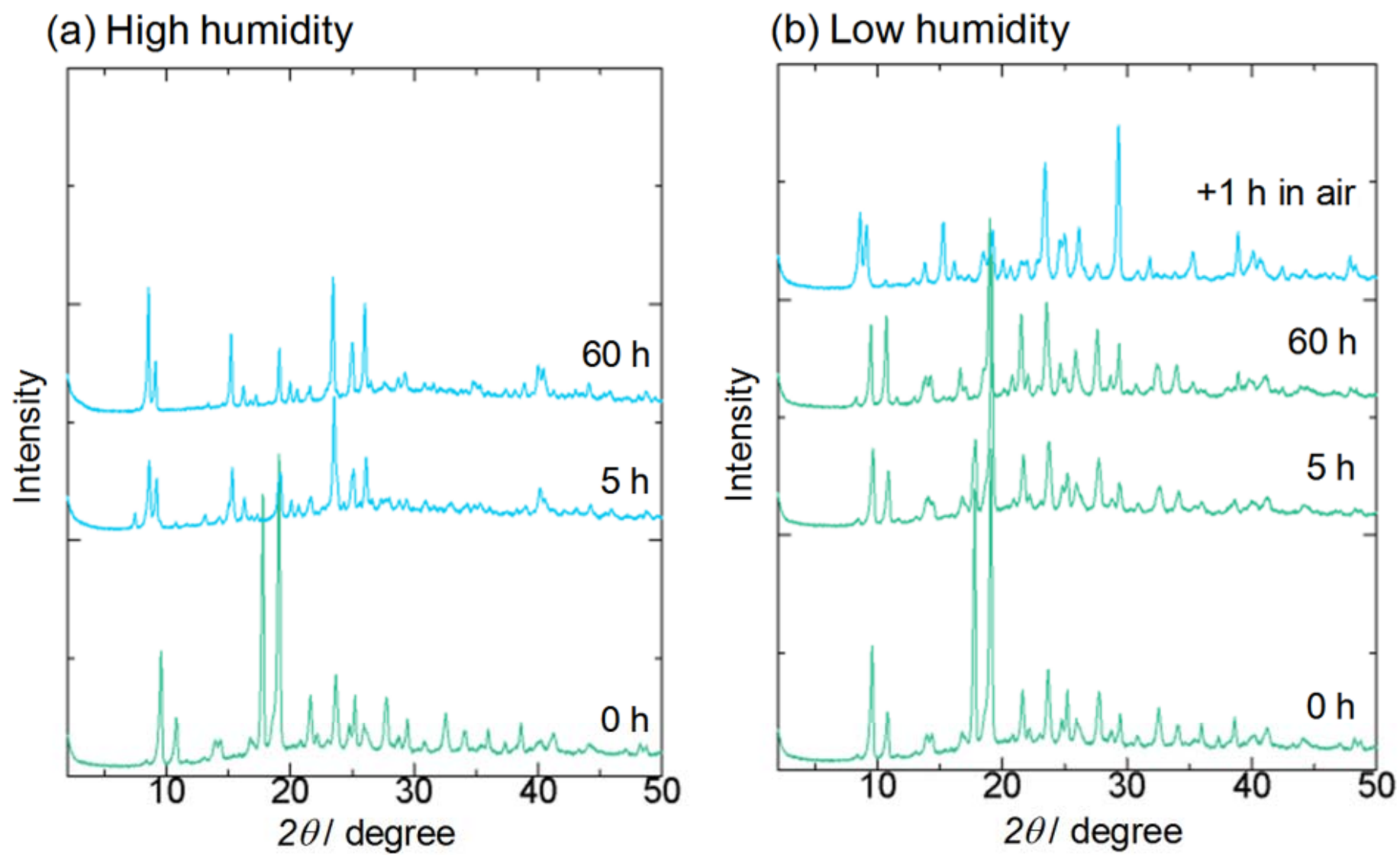


Fig. 3



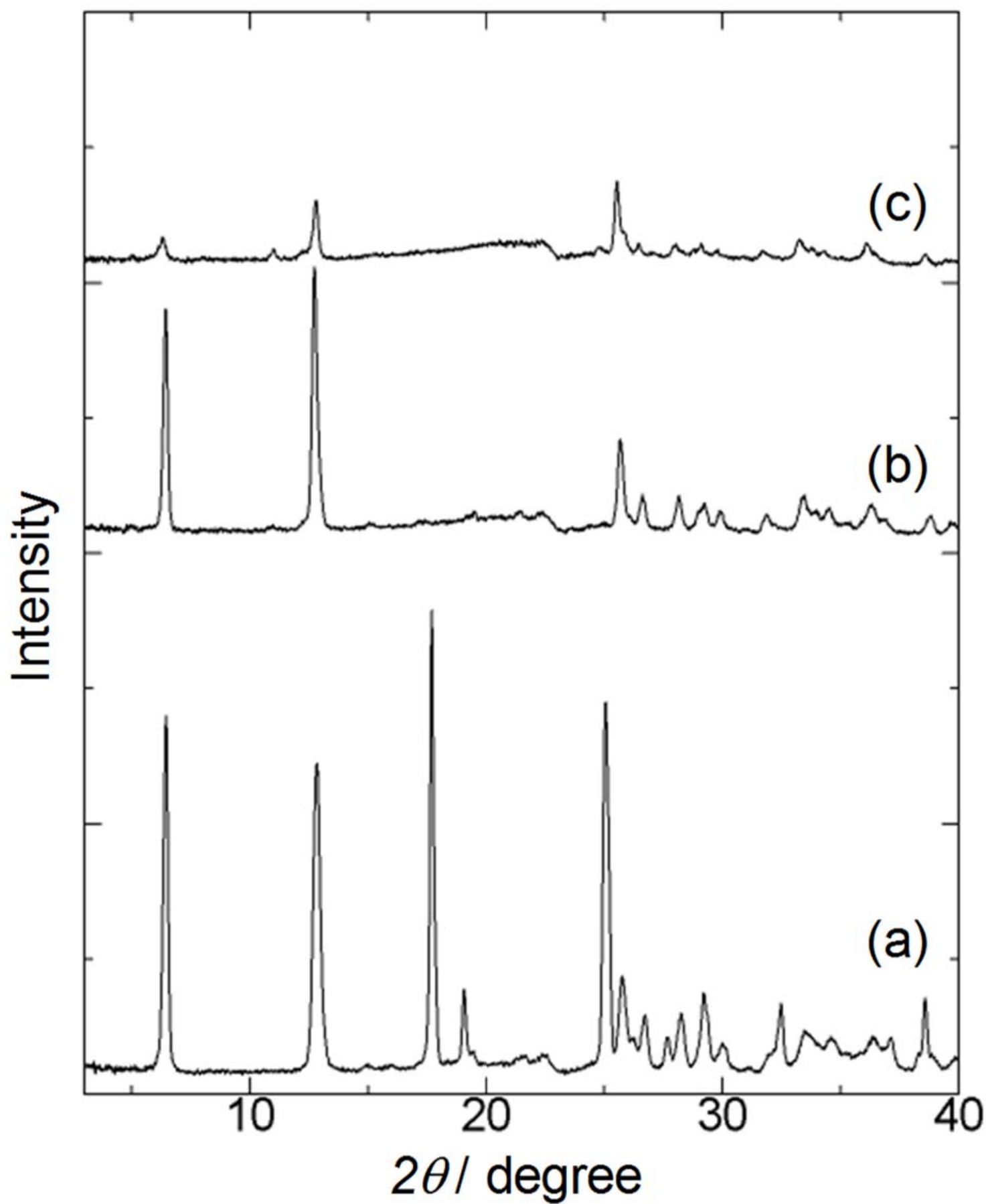


Fig. 5

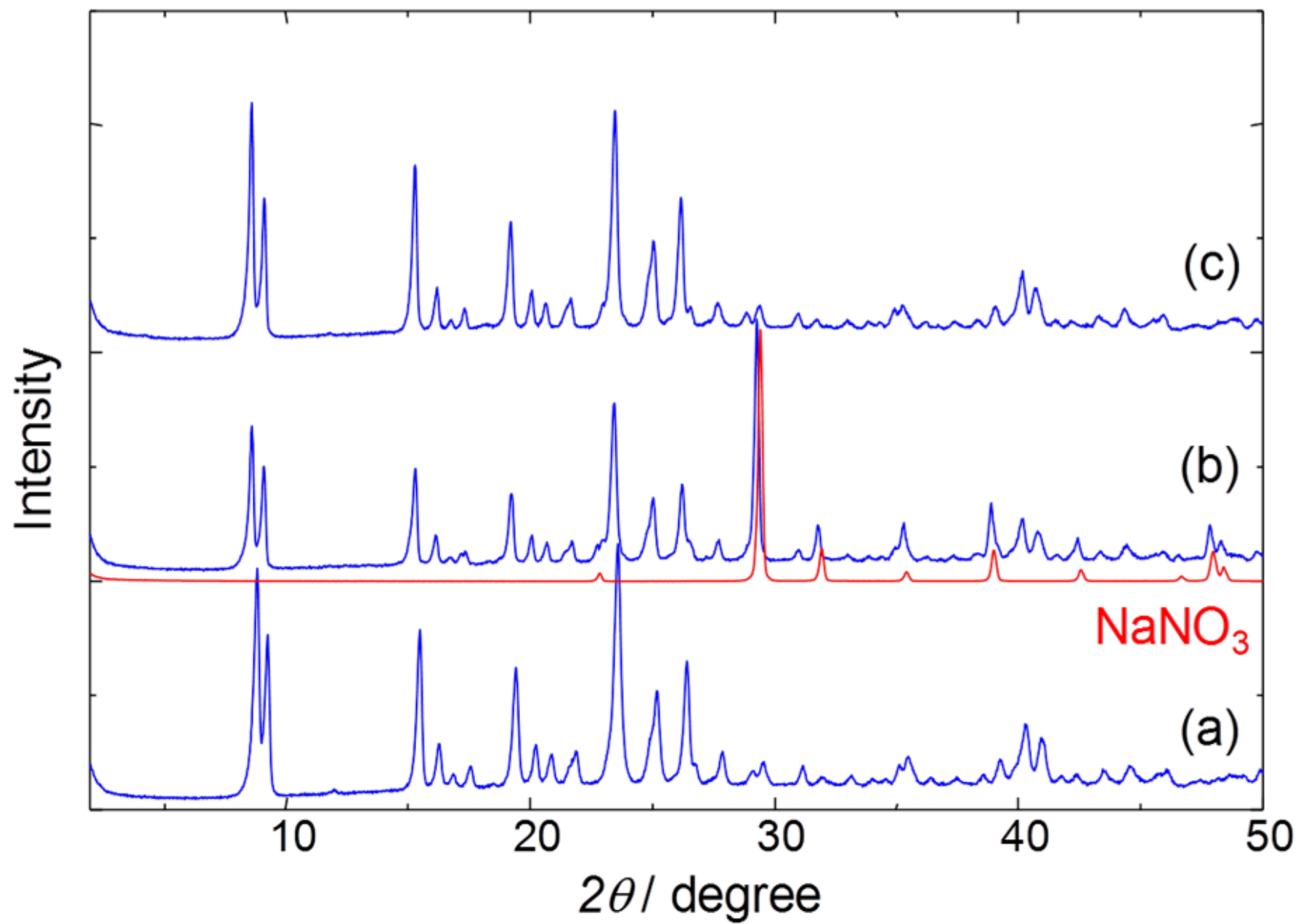


Fig. 6

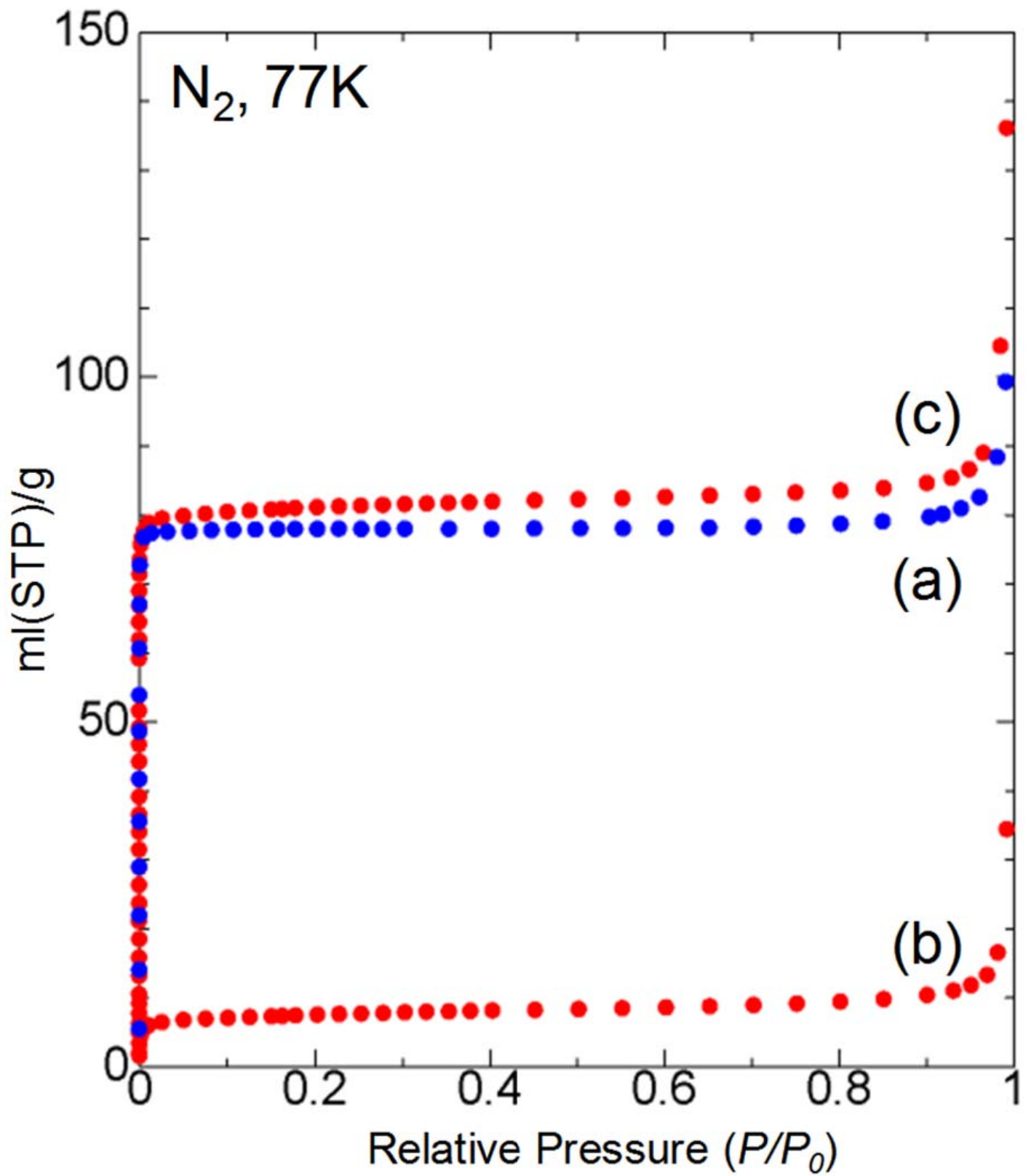


Fig. 7

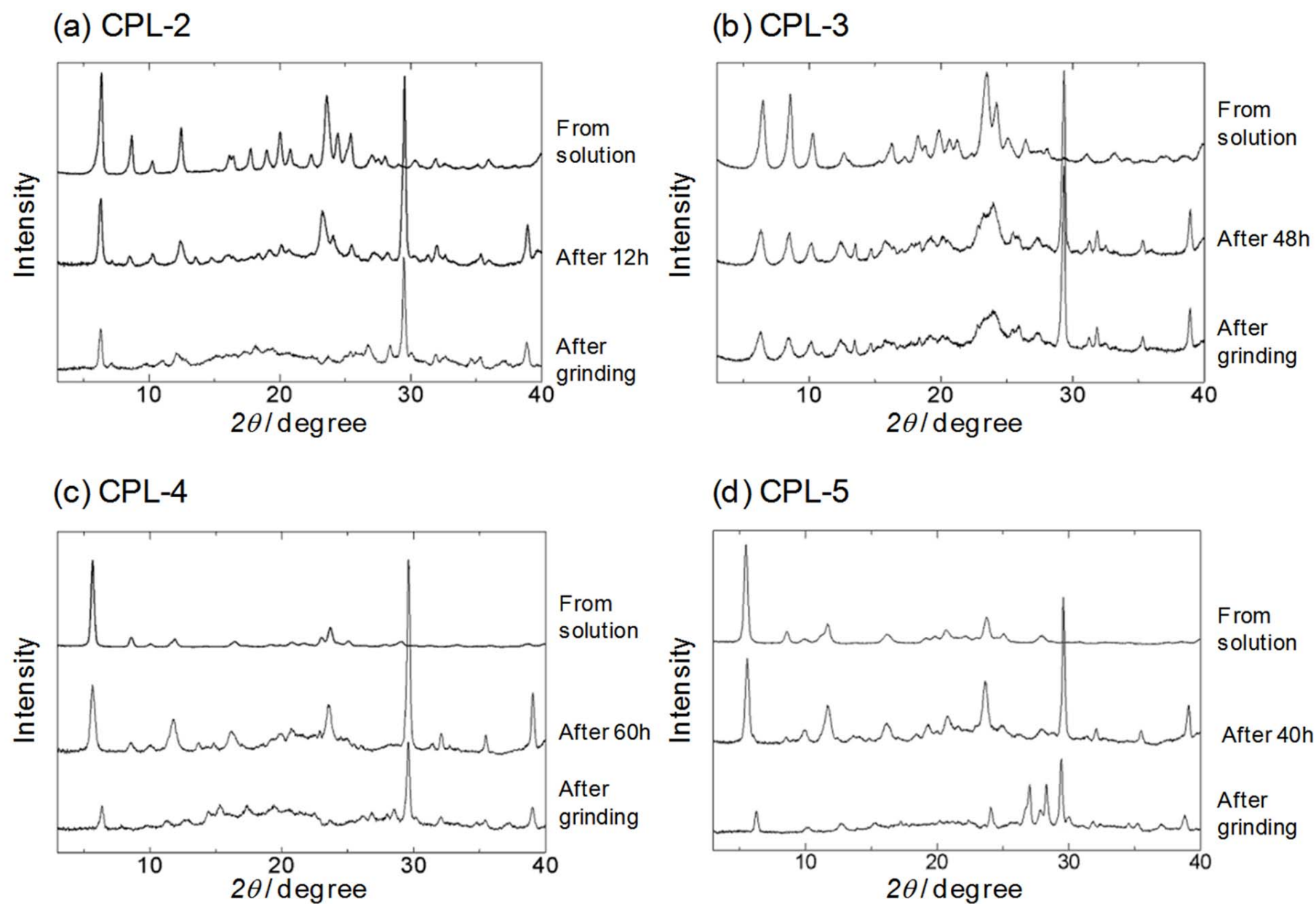
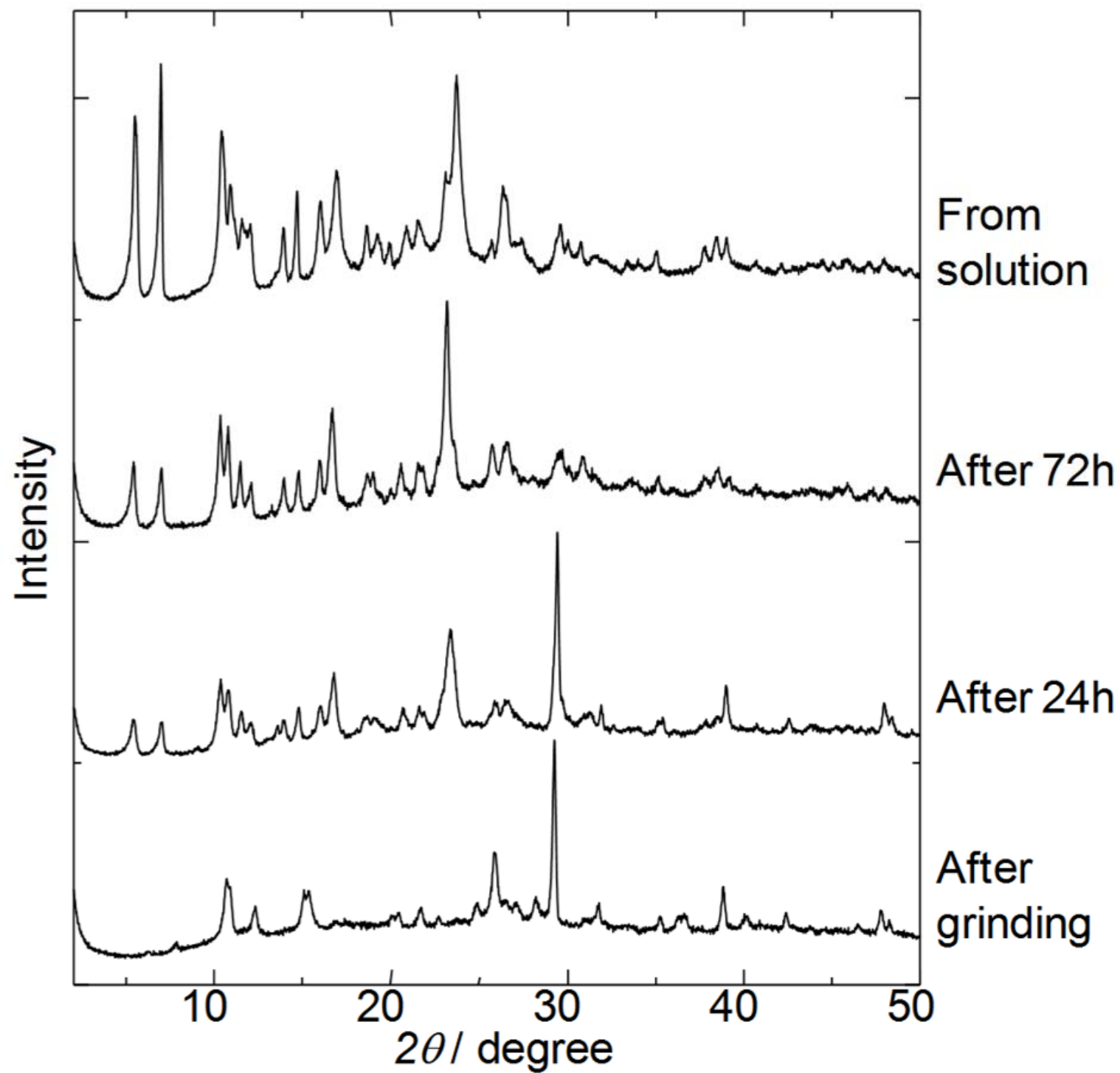


Fig. 8



Supporting information

“Systematic mechanochemical preparation of a series of coordination pillared layer frameworks”

Hirotooshi Sakamoto, Ryotaro Matsuda and Susumu Kitagawa*

Experimental Section

Materials

Solvent and starting materials for synthesis were purchased commercially, and were used as received. Preparations of CPLs in solution process were carried out according to the literature procedures.

Physical measurements

X-ray powder diffraction was carried out on a Rigaku RINT-2000 Ultima diffractometer with CuK α radiation ($\lambda = 1.54056 \text{ \AA}$).

The sorption isotherm measurements were performed by using an automatic volumetric adsorption apparatus (BELSORP-18; Bel Japan, Inc.). A known weight (100-200 mg) of the as-synthesized sample was placed in the quartz tube, then, prior to measurements, the sample was dried under high vacuum ($<10^{-2} \text{ Pa}$) at 383 K for 8 h to remove the solvated water molecules. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state.

Observation of time course of the transition, **M** to **CPL-1**

To investigate the transition behavior from **M** to **CPL-1**, time course of XRPD patterns of **M** was sequentially measured for 12 hours as shown in Fig. S1. As the measurements were proceeding, the peaks of the initial pattern were gradually decaying, and simultaneously the peaks of **CPL-1** were emerging. Although the transition had not completed after 12 h of the measurement, the sample quickly changed its color when taken out from the chamber of the powder diffractometer, and showed clear patterns of **CPL-1** within several hours left in air. After the sample was left in air for further 12 h, no more changes were observed in the patterns. We assumed that the difference in the transition rate was attributed to the humidity in the chamber or in air.

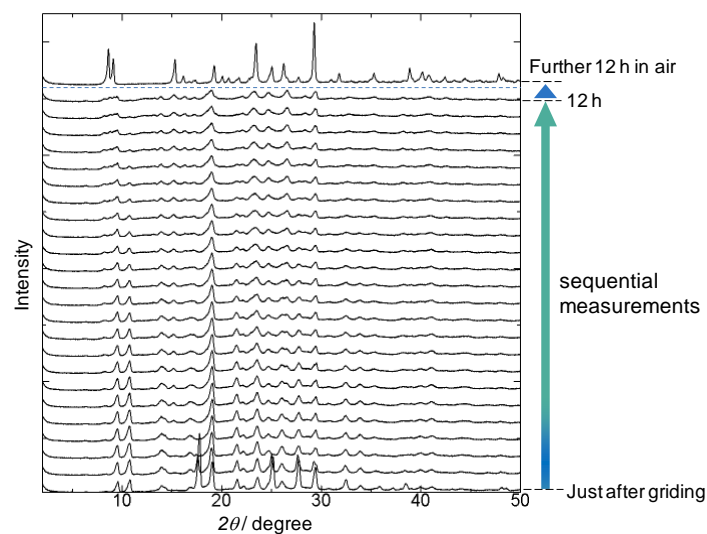


Fig. S1 Time course of XRPD patterns of **M** sequentially measured for 12 h (30 min per one measurement).

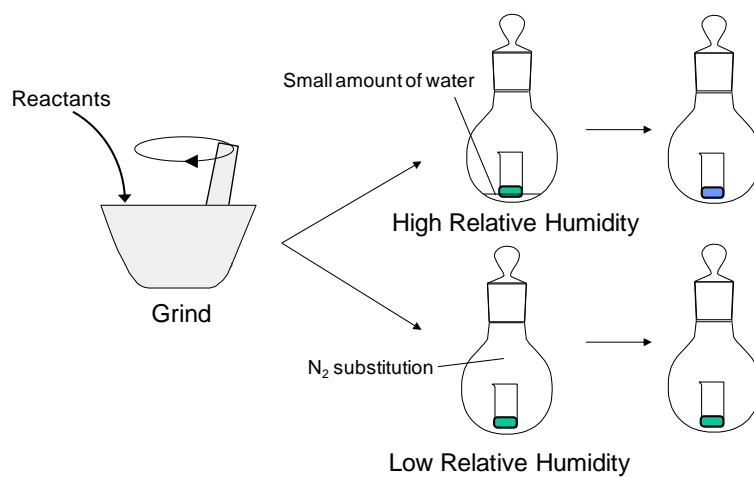


Fig. S2 Schematic illustration of the protocol in the humidity control experiment